Investigation of structure and transport in Li-doped ionic liquid electrolytes

[pyr14][TFSI], [pyr13][FSI], and *[EMIM][BF_4]*

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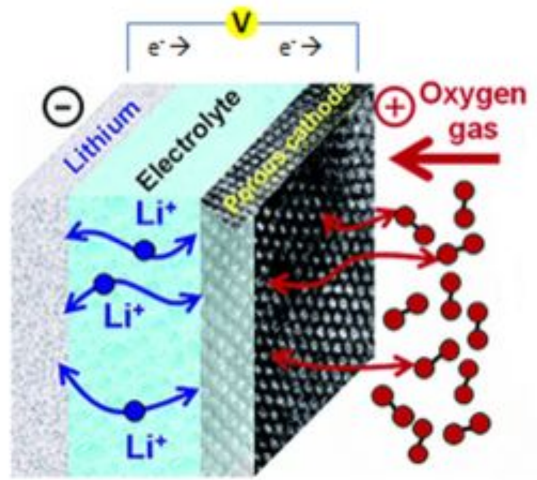
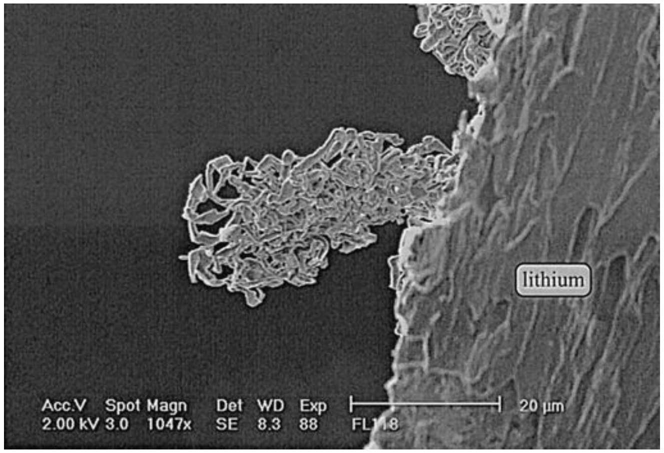
Ionic liquids for electrochemical applications

- **Advanced electrodes**: help stabilize cycling against Li-metal
- **Li-ion batteries**: possible safer alternative to organic electrolytes
- **Supercapacitors:** double layer capacitor electrolyte
- **Electrodeposition**: wide electrochemical window solvent
- **Biofuel cells**: replace water as more stable solvent



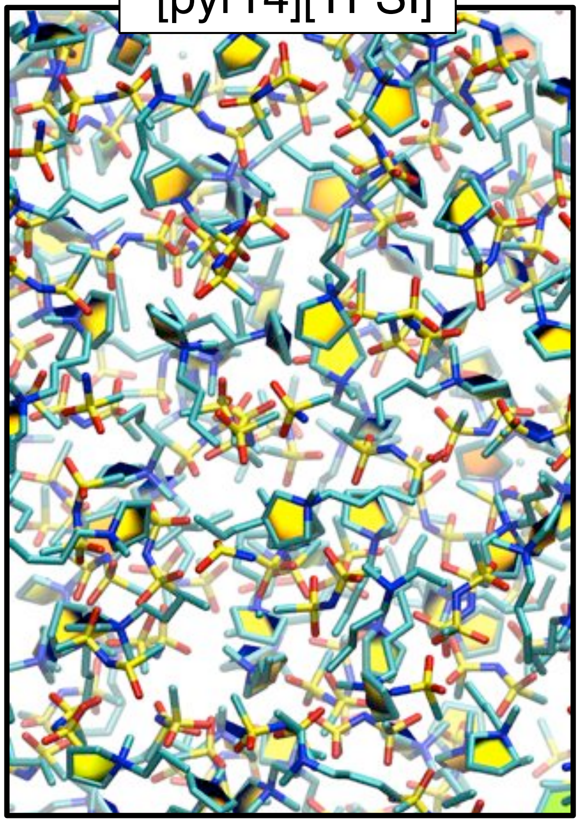


F. Orsini et al., J. Power Sources 76, 19-29 (1998)

Computational modeling of Li-doped ionic liquid electrolytes

- Comprehensive analysis of structure, thermodynamics, and transport
- Three distinct ionic liquid systems
- Six Li-doping levels (x_{Li}= 0 – 0.33)
- Four temperatures (T = 298 – 393 K)
- Polarizable force field
- Long simulation times (200 ns)
- Cross-checked with different codes

[pyr14][TFSI]



O. Borodin, *J. Phys. Chem. B* **113**, 11463 (2009)
O. Borodin, et al., *J. Phys. Chem. B* **110**, 6279-6292 (2006)
O. Borodin, et al., *J. Phys. Chem. B* **110**, 6293-6299 (2006)

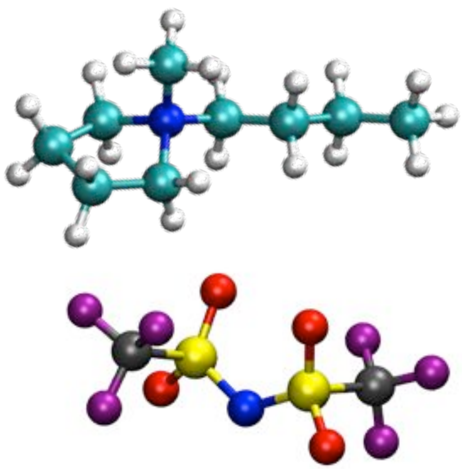
Outline

1. Li^+ solvation structure

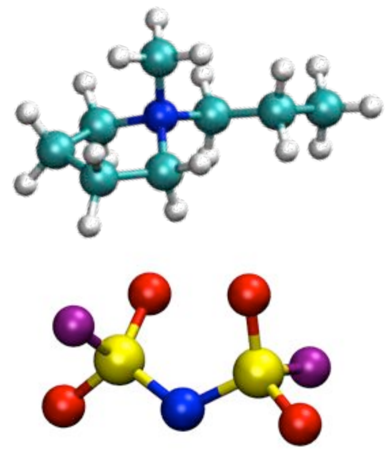
2. Transport properties

3. Li^+ transport mechanism

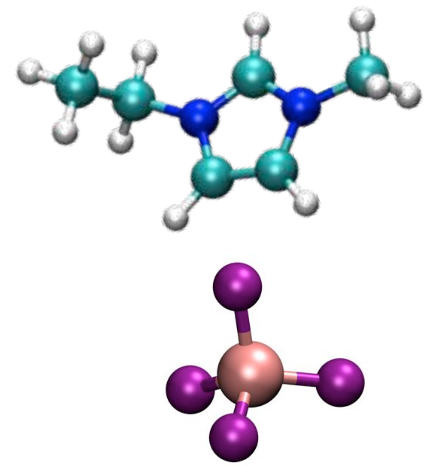
Ionic liquids



[pyr14][TFSI]



[pyr13][FSI]

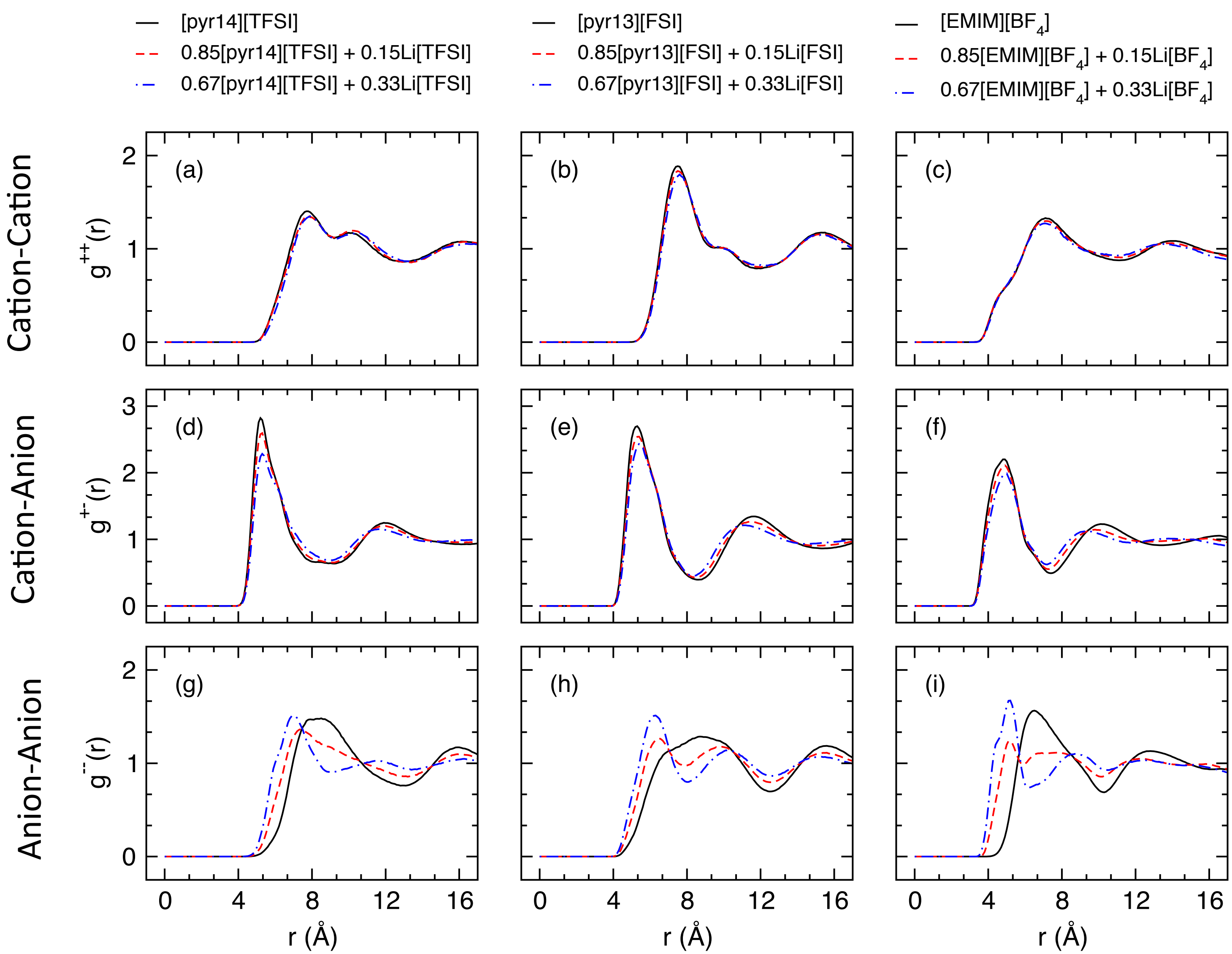


$[EMIM][BF_4]$

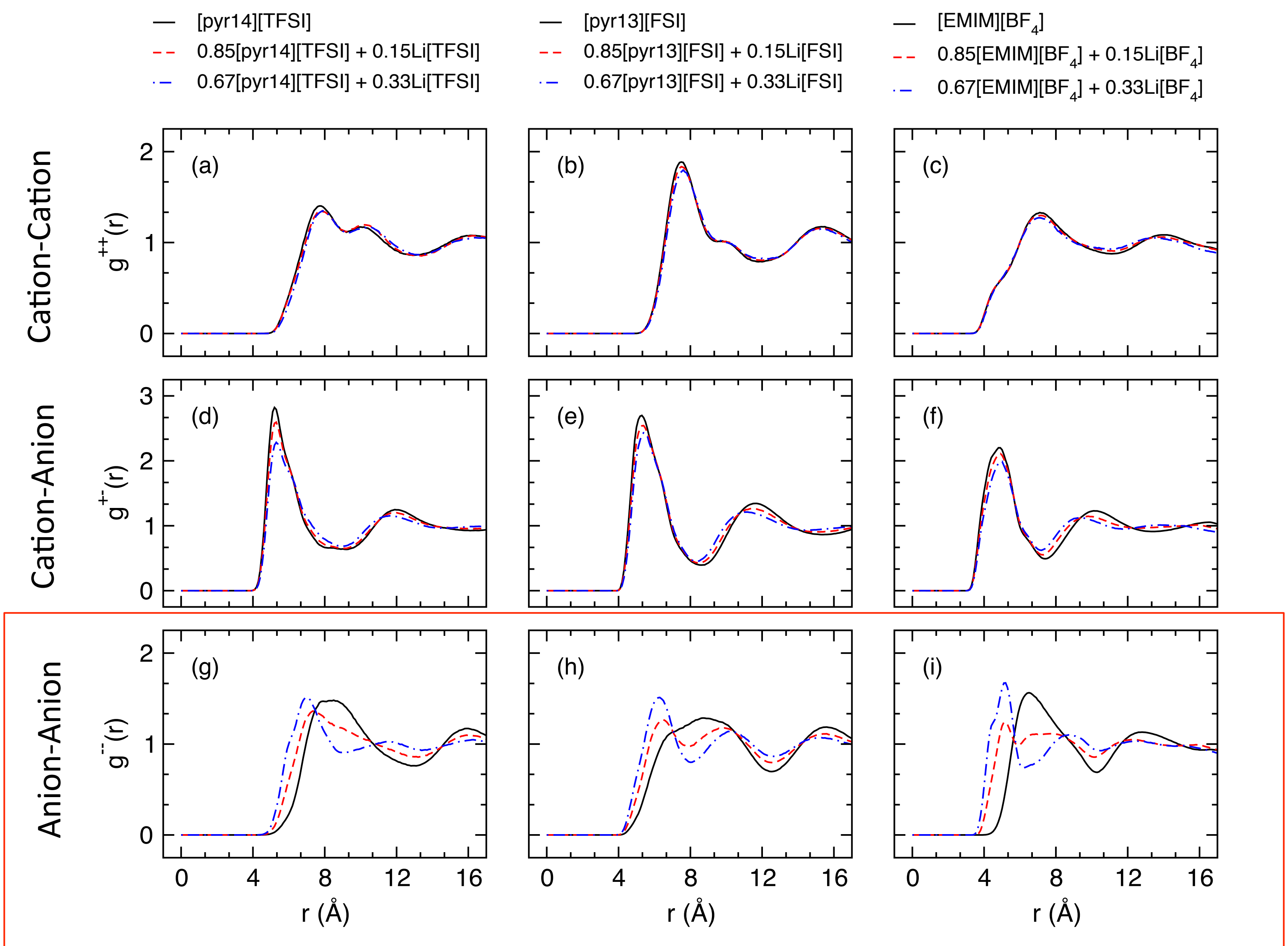
Chosen for supression of dendrites on Li^+ metal anodes[*]

Bhattacharyya et al., Nature Mater. (2010)
Basile, et al., Elechem. Commun. (2013)

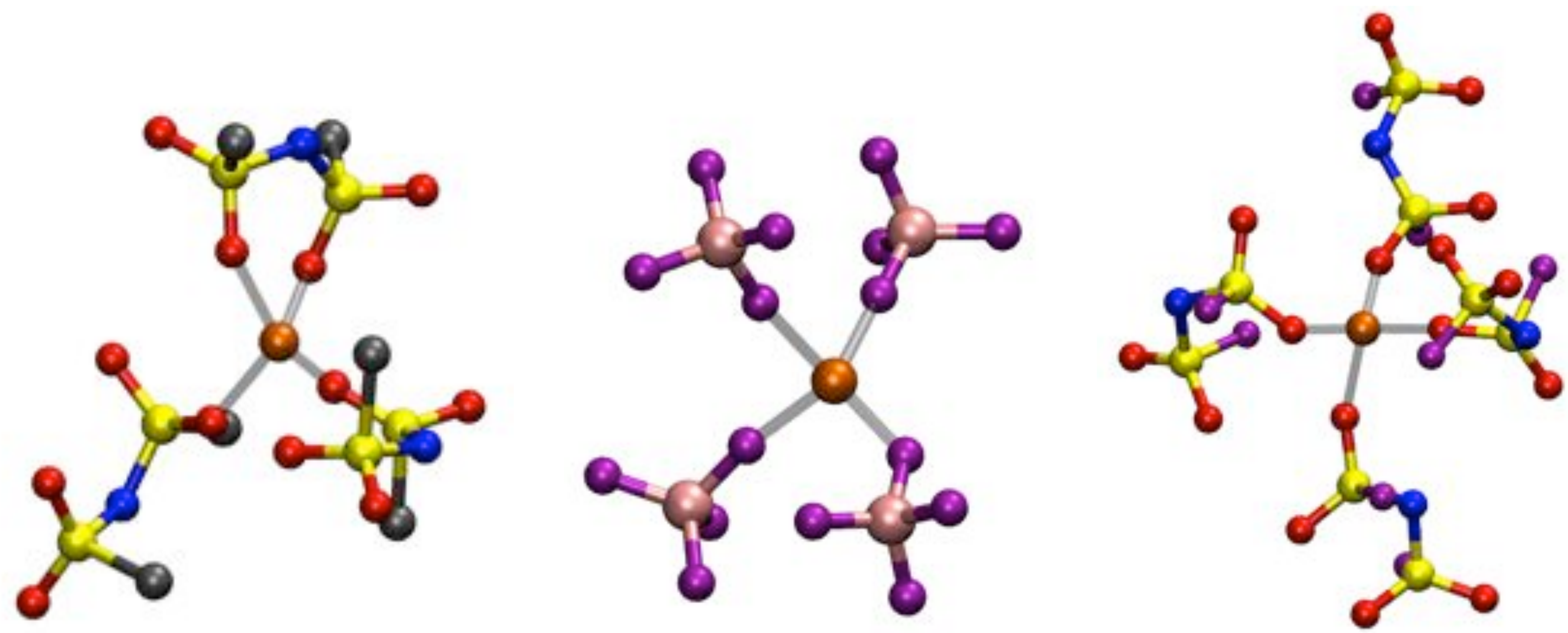
Radial distribution functions



Radial distribution functions



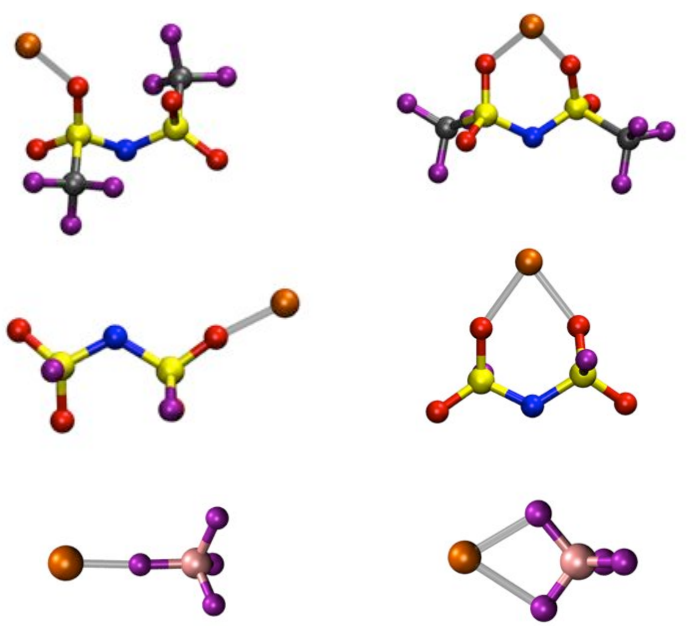
Solvation shells of Li⁺

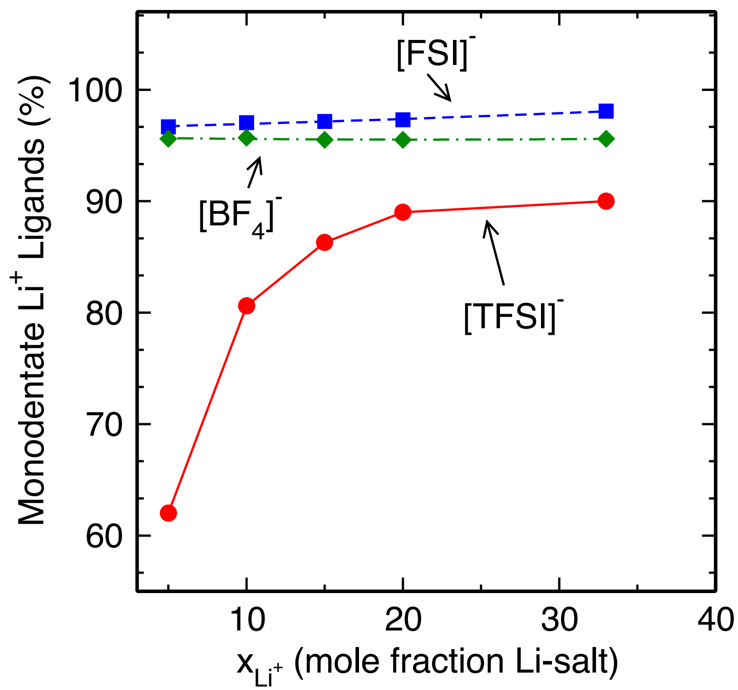


3 anion coordination for [TFSI] and 4 for [FSI] and [BF_4]

Li^+/Anion bonding

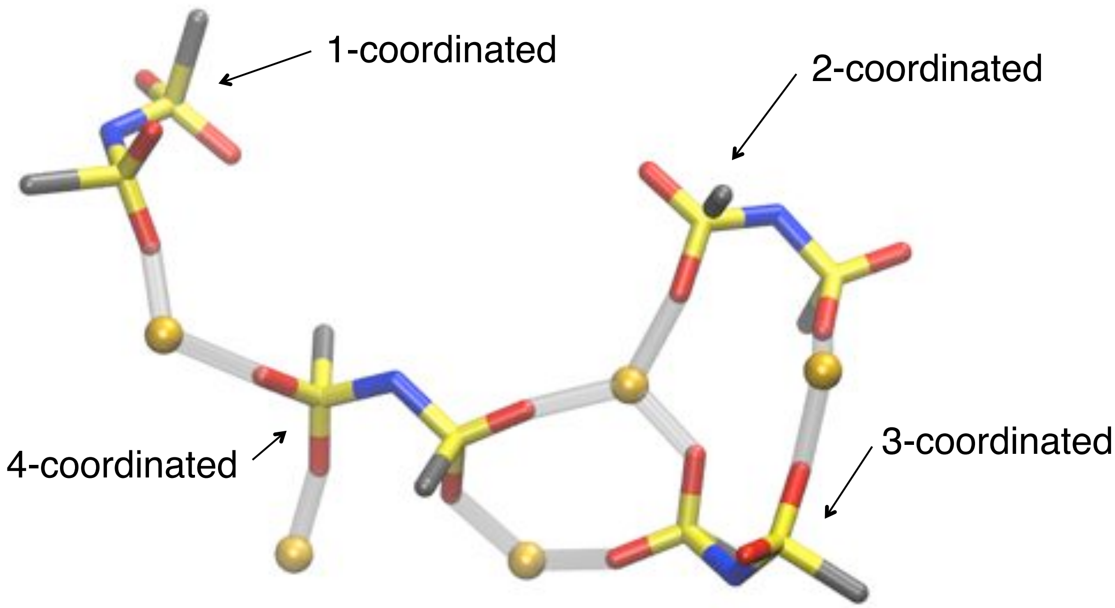
Monodentate (κ^1) Bidentate (κ^2)





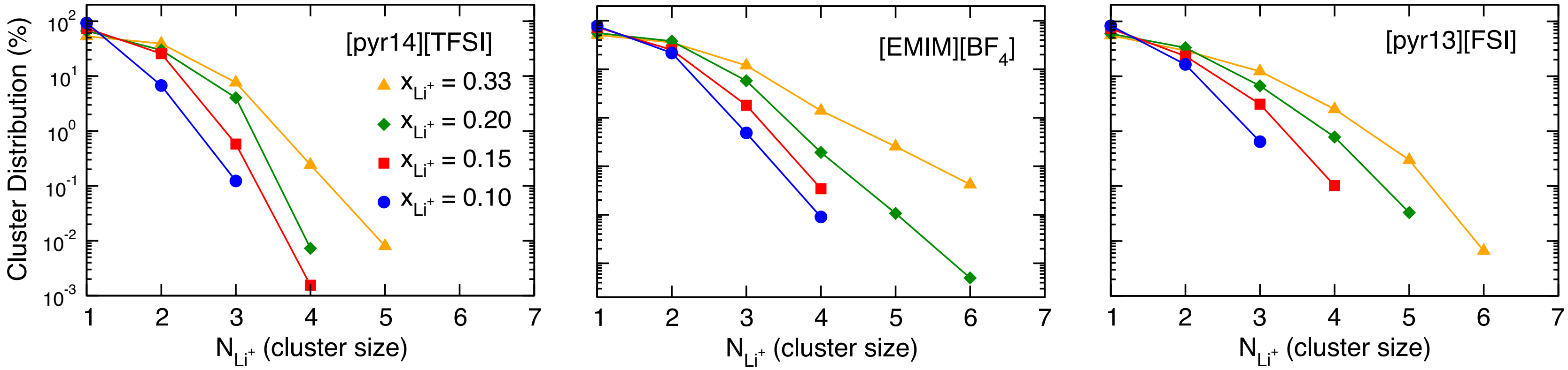
Monodentate bonding preferred at high Li-doping

Li^+ … Li^+ networks



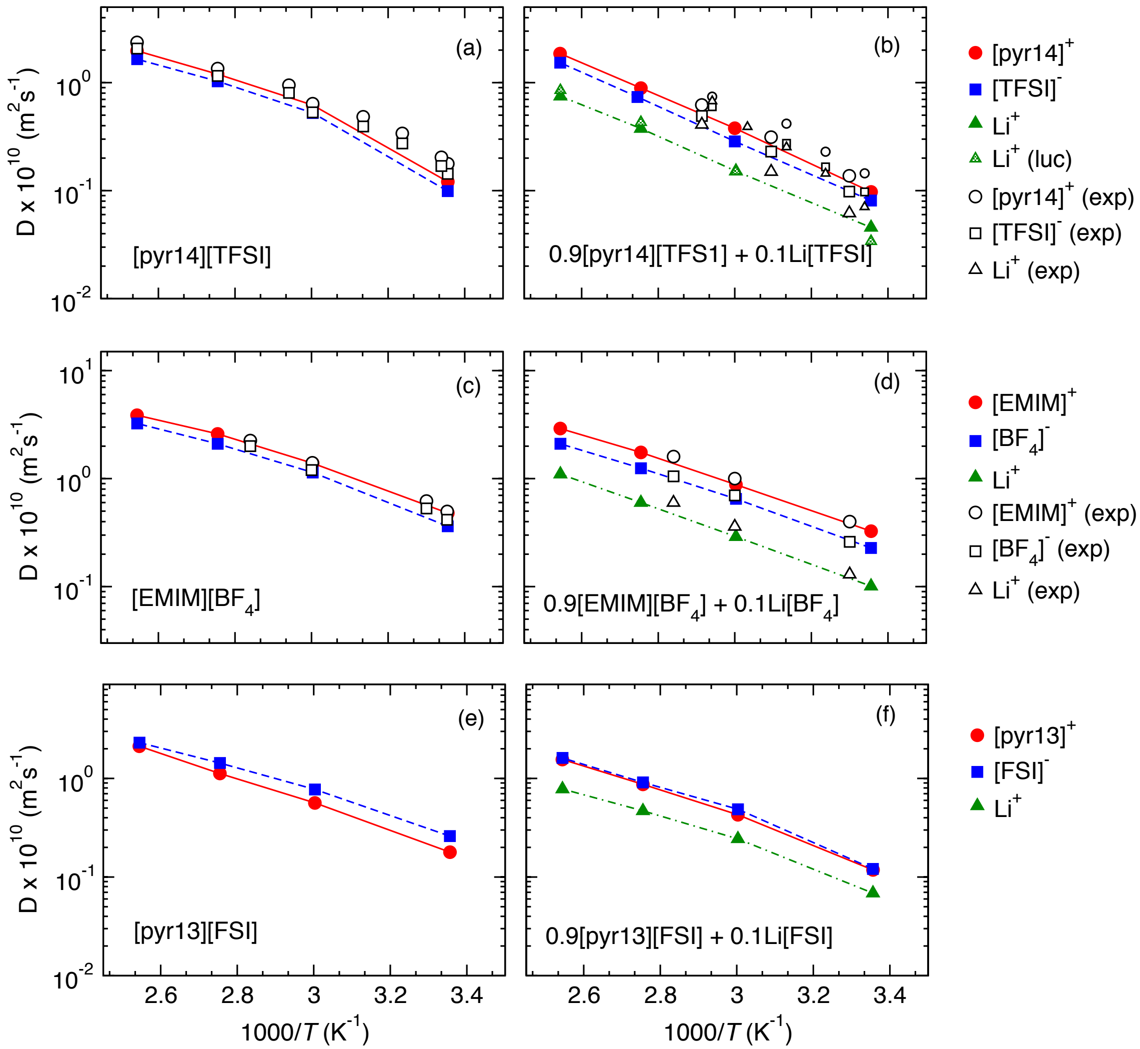
Network Li^+ share bridging anions

Li^+ … Li^+ networks



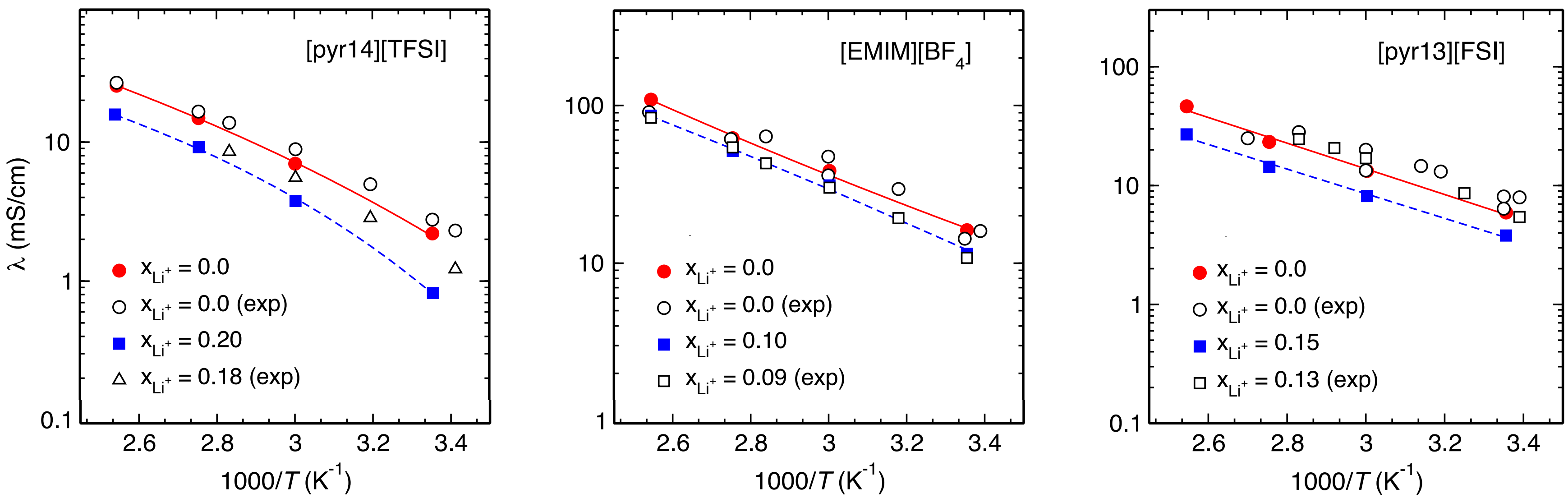
Li^+…Li^+ networks present at all levels of doping

Diffusion



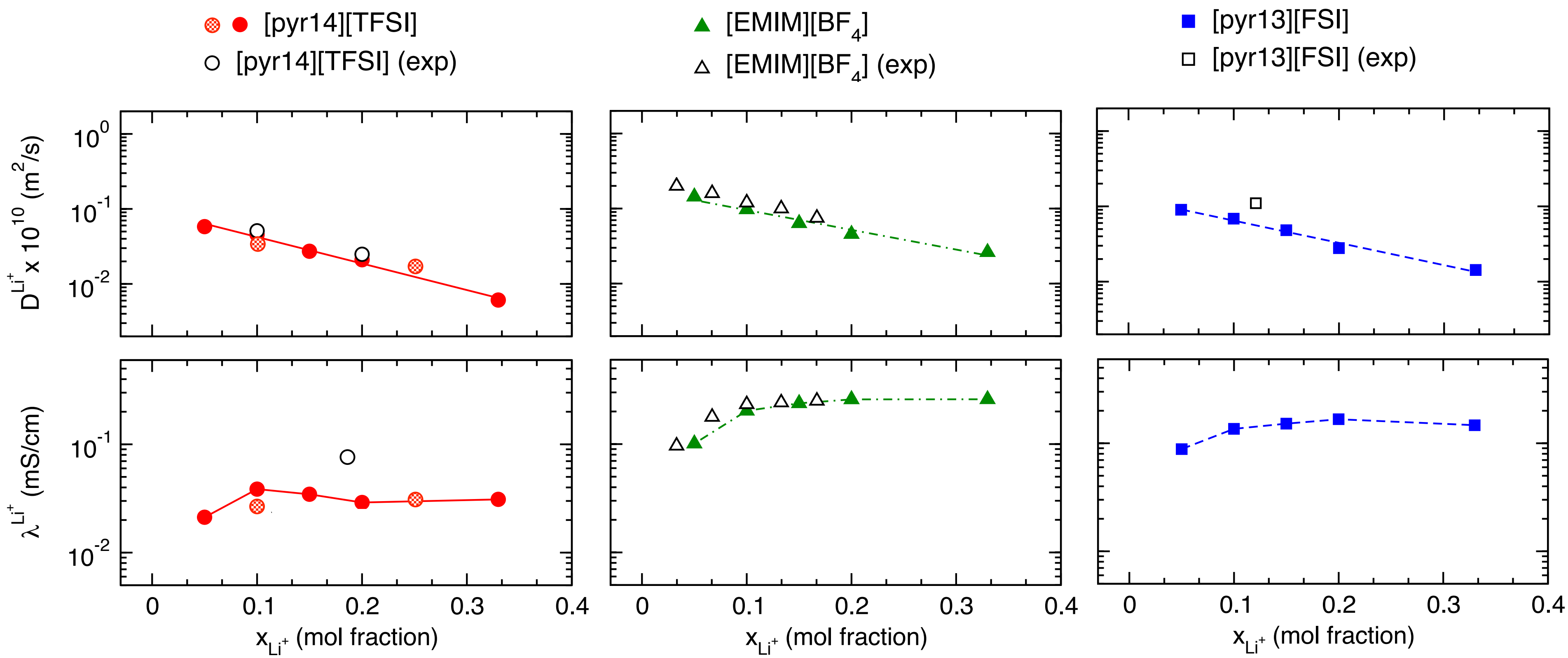
Li-doping suppresses diffusion of all ions

Ionic conductivity



Li-doping suppresses conductivity of all systems

Room-T Li transport



Li⁺ contribution to conduction plateaus at high salt doping

What is the mechanism for Li-diffusion?

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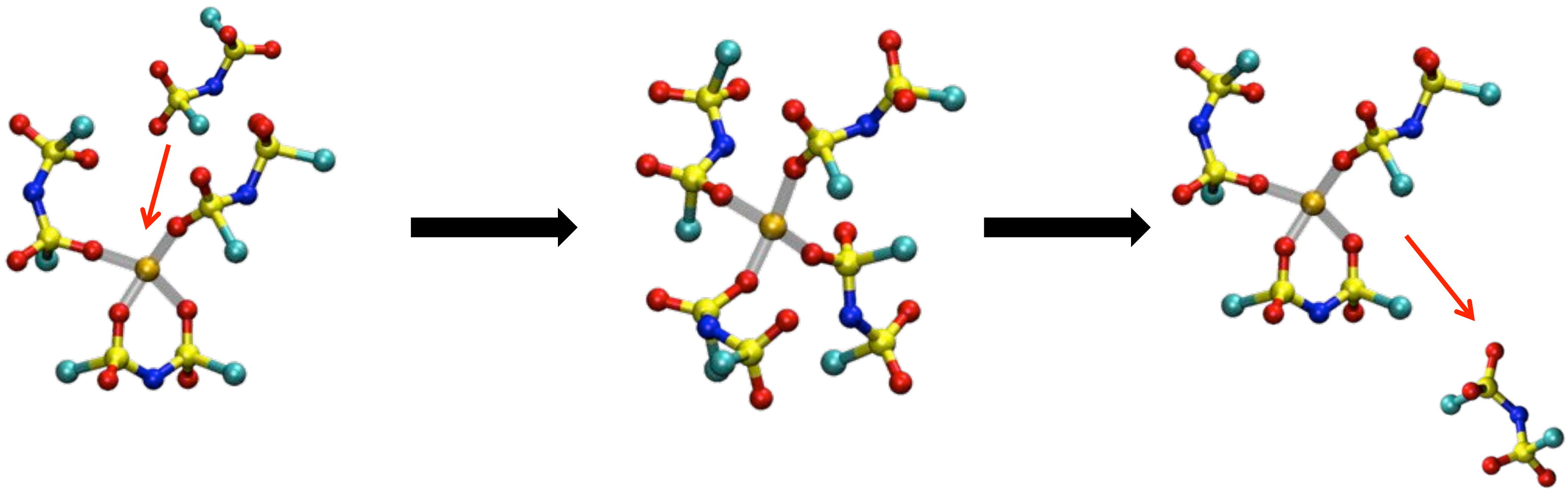
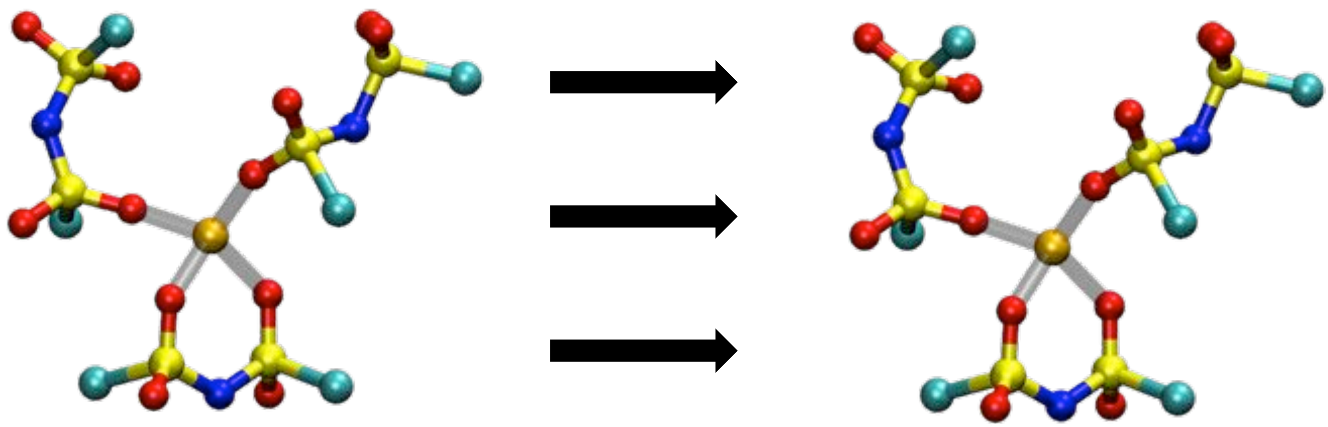


Anion Exchange

Hopping of Li^+ through exchange of anions

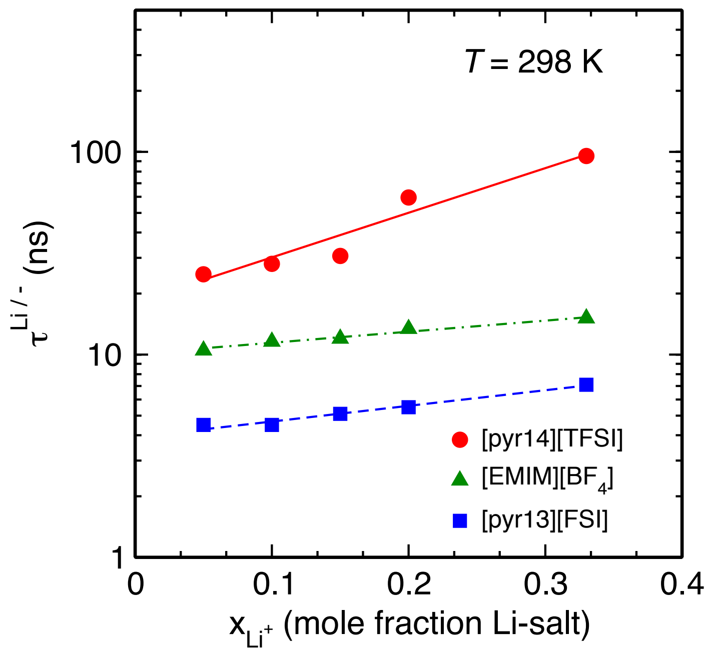
What is the mechanism for Li-diffusion?

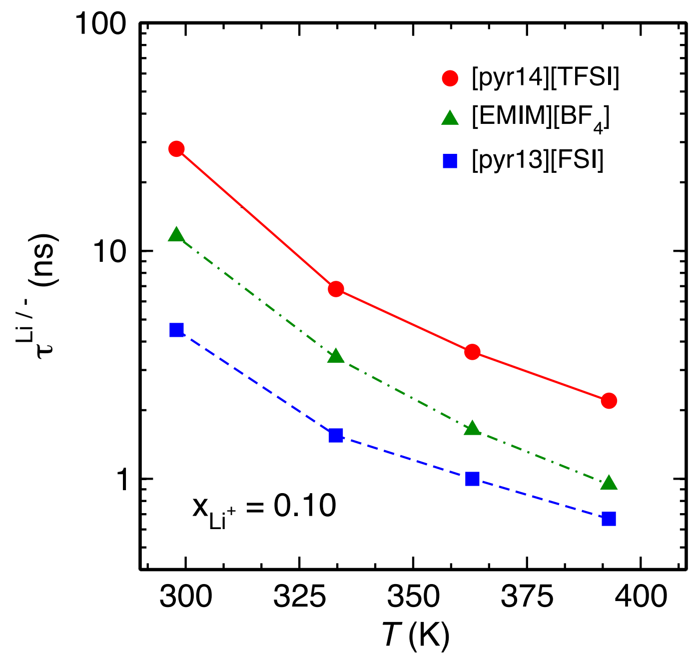


Vehicular

Net motion of Li^+ with the solvation shell

Li^+/Anion residence times





[TFSI] has longer residence times than other anions

Note: residence time of [TFSI] 30 ns at room-T

Room-T diffusion kinetics

	[pyr14][TFSI]	[pyr13][FSI]	[EMIM][BF_4]
x_{Li}	$\%D_{veh}$	$\%D_{veh}$	$\%D_{veh}$
0.05	69	81	89
0.10	66	85	107
0.33	59	73	91

Vehicular mechanism dominates the diffusion and increases in importance with decreasing anion size

Conclusions

- High Li-doping induces monodentate bonds

- Networks present at even low-levels of doping

- Transport properties in good agreement with experiment
  - Li^+ diffusion follows $[BF_4] > [FSI] > [TFSI]$
  - Li^+ conduction contribution plateaus at high doping levels

- Li^+ transport by anion exchange secondary to the vehicular mechanism

- Future work: properties at electrified interfaces

Haskins, et al J. Phys. Chem. B **118**, 11295 (2014) .

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